Hydration-Rind Dating of Basaltic Glass Artifacts: Reaction Dependence of Temperature and Chemistry

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INTRODUCTION

MARSHALL (1961) SUGGESTED THAT WATER molecules contained in glass are capable of breaking the Si-O-Si and Al-O-Al cross bonds by adding hydroxyl groups to an Si or Al atom. In 1966, Friedman et al. suggested that perlite (hydrated glass from obsidian) can form during diagenesis at measurable rates and applied Fisk's Law to describe the depth of water penetration as a function of environmental temperature at given glass compositions. In 1969, Morgenstein described the alteration process of palagonitization from sideromelane (basaltic glass) and developed a linear reaction, base-exchange-limited, which conformed to observed products during halmyrolysis (ocean weathering).

Morgenstein and Riley (1975:152) described an empirical method for obtaining a "general" rate of hydration for basaltic glass (sideromelane) in Hawaii and have related that method to the theoretical development of hydration of acid glass (obsidian). More recently, Jakobsson and Moore (1986) reported empirical rates of hydration of basaltic glass based upon measured temperature and palagonite rinds at Surtsey volcano, Iceland. Their data shed light on the earlier work of Morgenstein and Riley (1975).

Morgenstein (1969) showed that the hydration of basaltic glass in deep-sea sediments at temperatures approximating 5 °C was 2.91 microns-per-thousand years (approximately 0.003 microns-per-year). Hekinian and Hoffert (1975) obtained a hydration rate of 0.003 μm-per-year (3.0 μm-per-thousand years) for sideromelane to palagonite transition for deep-sea Atlantic rift zone samples at temperatures of approximately 4 °C. The Atlantic data were acquired by fission-track dating of basalt samples. Submarine basalts and basaltic glass are fairly uniform in chemical composition (Table 1). Deep ocean bottom-water temperatures and for the most part water composition are also quite invariant; consequently, ocean-floor volcanics provide reasonable natural controls on the variables affecting volcanic-glass hydration. For these reasons and the agreement of rates of basaltic-glass hydration in the literature, a hydration rate for ocean-floor sideromelane of 0.003 μm-per-year at 4 °C is assumed to be a reasonable and valid value.

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TABLE 1. CHEMICAL ANALYSES OF BASALT AND BASALTIC GLASS

	SOUTH PACIFIC	ATLANTIC OCEAN	MID-ATLANTIC RIDGE	HAWAII	SURTSEY
SiO_2	46.76	49.54	47.55	47.01	47.1
Al_2O_3	17.71	16.47	13.94	12.12	16.6
Fe_2O_3	1.73	2.30	4.31	2.86	—
FeO	10.92	7.55	9.15	0.29	12.1*
MnO	0.44	0.19	0.21	0.17	0.3
MgO	10.37	7.91	6.15	12.61	5.3
CaO	11.56	11.43	10.85	8.98	9.9
Na_2O	1.83	2.62	2.59	2.36	3.90
K_2O	0.17	0.30	0.20	0.72	0.71
H_2O^+	—	0.95	2.15	0.66	—
H_2O^-	—	0.27	0.43	0.41	—
TiO_2	—	—	2.63	0.48	2.60
P_2O_5	—	—	0.24	0.27	—

Note: The South Pacific, Atlantic Ocean, Mid-Atlantic Ridge, and Hawaii data are from Morgenstein and Rosendahl (1976:142, Table 8.1). The Surtsey data are from Jakobsson and Moore (1986:652, Table 1).
*Total Fe as FeO.

Jakobsson and Moore (1986:650) reported that the rate of palagonitization doubles for every 12 °C temperature increase at the Surtsey site. If this thermal control on basaltic-glass hydration is universal (for basaltic glass) then it may be possible to calculate a hydration-rate for various temperatures in Hawaii. We used the Jakobsson and Moore (1986) rate–temperature relationship with a fundamental hydration rate of ocean-floor sideromelane to arrive at the following (see Fig. 1):

Ocean floor: 4 °C with a rate of 0.003 microns-per year
Hawaii: 16 °C with a rate of 0.006 microns-per-year
Hawaii: 28 °C with a rate of 0.012 microns-per-year.

The above rate calculated for 28 °C corresponds well with the rate (0.0118 microns-per-year) of 11.77 microns-per-thousand years (at about 24 °C) reported by Morgenstein and Riley (1975). These data are compelling evidence that the rates used in hydration-rind dating of basaltic glass in Hawaii are generally valid on the basis of empirical evidence (see Table 1 for chemical analyses of Pacific, Atlantic, and Hawaiian basalt and basaltic glass compositions). The 11.77 μm-per-thousand years rate determined by Morgenstein and Riley (1975) did not empirically measure the effective environmental temperature. A temperature of 24 °C was determined as being the reasonable average effective temperature for Hawaii. It is recognized that these data need to be refined. The new curve developed here (Fig. 1) may serve that purpose.

Jakobsson and Moore (1986) also reported that the rate of hydration of sideromelane to palagonite is about five times greater at Surtsey than reported for ocean glasses at similar temperatures. Consequently, temperature cannot be the only controlling parameter for hydration-rate determination. Charles (1958), among others, recognized that the water-diffusion mechanism in glass is autocatalytic, suggesting that the actual transport process is a function of diffusional characteristics (Marshall [1961] and Friedman et al. [1966]) *and* variable reaction characteristics, which are dependent upon glass composition

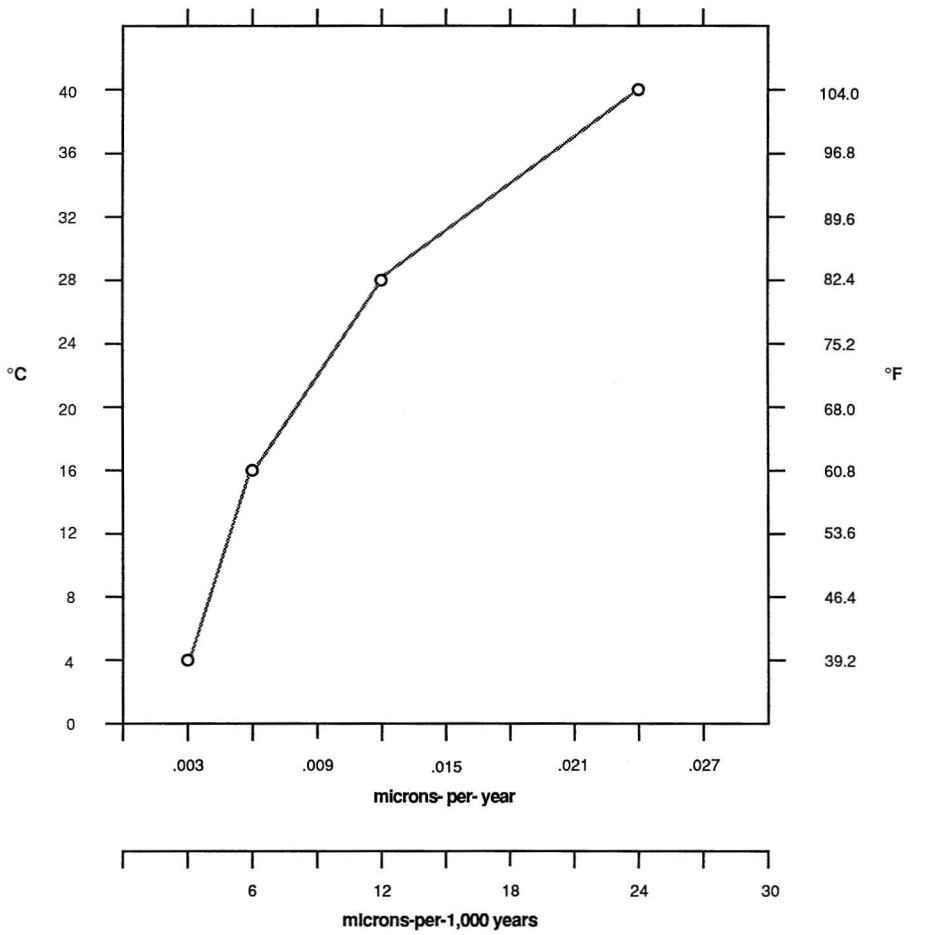

Figure 1. Basaltic glass hydration rates as a function of temperature. Rate of glass hydration based upon data from Jakobsson and Moore (1986) and Morgenstein and Riley (1975). For basaltic glass of chemical composition similar to Ocean Dredge Sample A150-RD8 see Morgenstein (1969) and Morgenstein and Riley (1975).

and characteristics of the diffusing species. Cerling et al. (1985), in their studies of low-temperature alteration of volcanic glass, have determined that molecular water (H-O-H) is clearly dominant over hydroxyl groups. Their data indicate that the relative speciation of water in high- and low-temperature glasses is different.

Low-temperature glass is defined here as being most probably below 60 °C (Cerling, pers. comm. 1988). These data also demonstrate the differences in reaction kinetics under different temperature regimes. Therefore, it is not compelling to rely on high temperature experimentation for the prediction of low temperature hydration reactions. At present, the temperature where bonding speciation changes is not well defined. In addition, speciation probably changes in a gradational manner rather than abruptly. Consequently, the modeling of the behavior of glass hydration needs to await a more precise resolution of the reaction kinetics and the resulting bonding speciation for a variety of temperature and glass compositions. Cerling et al. (1985) further state

> The early low-temperature alteration of volcanic glass of peralkaline affinity by meteoric water involves ion exchange, hydration, and oxygen and hydrogen isotopic exchange. In [our] study, up to 40% of the alkali cations (NA + and K +) could be replaced by H + ions with no measurable change in the bulk composition of the glass or in the distribution of minor and trace elements, excepting other alkali ions such as Rb + . (p. 291)

The above indicates that alkali exchange in low-temperature glass is one controlling parameter for hydration (the greater the alkali concentration, the greater the rate of exchange and therefore the greater the overall rate of hydration). It is suggested, then, that both glass and pore-water composition are vitally important in hydration-rate control.

Jakobsson and Moore (1986:652, Table 1) report chemical analyses of Surtsey sideromelane. Their data indicate that Surtsey glass as compared to Ocean Rift glass (Morgenstein and Riley 1975) is about 30 percent higher in sodium oxides, similar in potassium oxide, and lower in calcium and magnesium oxides (Table 1). The Ocean Rift zone glasses are similar to glasses from Mauna Kea (Morgenstein and Rosendahl 1976:142, Table 8.1) (see Table 1). On this basis alone (the variable composition of Surtsey and Hawaiian sideromelane), we might anticipate a difference in the rate of hydration between the two glasses. In addition, the Surtsey site contains halite (NaCl), which may be evidence of an elevated alkali cation content in pore water. If we consider autocatalytic exchange driven by alkali ions in the pore water, the higher the alkali content of the hydrating fluids, the more rapid the rate of hydration. Thus, it is reasonable to assume that the Surtsey site would produce elevated rates of hydration over that which may be experienced in environments with less alkali cation pore-water concentrations and lower sodium concentrations in the glass itself.

Although the above arguments are theoretically consistent, other interpretations are plausible. The evidence that alkali cation contents of pore water and glass play important roles in controlling the rates of hydration of basaltic glass indicates that data need to be acquired on a site-by-site basis in order to ascertain the effects on the hydration rate. Consequently, until there is better geochemical control and understanding of the hydration of basaltic volcanic glass, the hydration-dating method should be utilized with care. The method should not be relied on for absolute chronologies and should be used in combination with other dating methods.

CONCLUSION

As Cerling et al. (1985) have determined that speciation of water in high- and low-temperature glasses is different, and Charles (1958), among others, has recognized that glass composition and the diffusing species control the hydration phenomena, it becomes important to recognize the differences and similarities between obsidian and sideromelane. Friedman et al. (1966) indicate that a quadratic expression of diffusion adequately describes the behavior of the obsidian to perlite transition. Morgenstein (1969) characterizes the hydration process of sideromelane as being linear. These differences in behavior can be attributed to the marked differences in glass chemistry and therefore network former and modifier bonding and corresponding response of alkali cation exchange during hydration as well as solution or matrix breakdown and related reactions. By increasing the amount and/or basicity (Na to K) of the alkali, the quantity of bonded molecular water is increased (Scholze 1966, Cerling et al. 1985). With this increase in the alkali content of glass (or basicity of the alkali content), the diffusion rate increases.

There is good evidence for looking at more than one mechanism or reaction style with respect to glass hydration. Each of these reactions (base exchange and solution-corrosion/matrix breakdown) proceeds at its own initial rate. Other reactions, such as the hydration of iron oxide, may serve to drive the base exchange and solution reactions at a more elevated rate. It appears that the mafic glasses (sideromelane) react more rapidly than the acid glasses (obsidian) because they have more potentially reactive components (such as iron). By applying higher temperatures to the system, the reaction rates are elevated. Jakobsson and Moore (1986) show that a temperature increase of 12 °C doubles the rate of hydration for sideromelane. As the temperature and the rate of reaction are increased, the bonding style of water changes and the diffusion-limited characteristics become more and more dominant. At high temperatures, therefore, a quadratic expression best describes glass hydration reactions. Consequently, experimental work at elevated temperatures investigates reactions that are certainly different than those occurring at ambience and which, therefore, should not be unequivocally used to describe lower temperature *in situ* reactions.

Glasses from archaeological settings may transcend periods of climatic change and be exposed to variations in temperature due to sedimentary burial and changes in environmental chemistry caused by fluctuations in the hydrogeologic regime. Measurements of the present-day soil temperature profile and its pore-water chemistry are not necessarily representative of thermochemical fluctuations through time, and therefore a glass artifact may exhibit a history of hydration-rate variations through time. The choice of the rate of hydration for use is therefore subjective even though site-specific information may be collected. For these reasons, it becomes imperative that the hydration dating technique be used in conjunction with other methods and that site-specific data be collected prior to determining specific hydration rates.

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